CERTIFICATE

I, Futoshi HAYAKAWA, c/o KYORITSU INTERNATIONAL, 3-2-5 Meieki, Nakamura-ku, Nagoya-shi, Aichi-ken, Japan, hereby solemnly and sincerely declare:

(1) THAT I am well acquainted with the Japanese language and English language, and

(2) THAT the attached translation is a true and accurate translation into the English language of the official copy of the document in respect of an application for a Japanese Unexamined Patent Publication No. 01-092377 published in Japan on the 11th day of April 1989, and of the official certificate attached thereto.

Futoshi Hayakawa

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Signed this 8th day of August, 2008

PATENT ABSTRACTS OF JAPAN

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Description

1. Title of the Invention

Method of pretreating electroless plating material

2. Claims

[Claim 1]

A method of pretreating an electroless plating material, which is performed before an electroless plating method in which a synthetic resin molded product is used as a material, and a metallic film is deposited on the surface of the material by chemical treatment, wherein, before the electroless plating, the material is treated with ozone while being heated.

[Claim 2]

The method of pretreating an electroless plating material according to claim 1, wherein the material is treated with ozone while being heated, under the ultraviolet irradiation.

[Claim 3]

The method of pretreating an electroless plating material according to claim 1 or 2, wherein the material treated with ozone is washed with sulfuric acid.

3. Detailed Description of the Invention

[Technical Field]

[0001] The present invention relates to a method of pretreating a synthetic resin molded product before the electroless plating of the synthetic resin molded product.

[Background Art]

[0002] Generally, electroless plating, which is a method of forming a metallic film on a subject material by reducing metal ions in a solution into a metallic precipitate using chemicals, is different from electroplating, in which the metallic film is formed by creating a metallic precipitate using an external power supply. In electroless plating, a metallic film can be formed even on an insulating material, and the electroless-plated insulating material can also be electroplated, so that, recently, electroless plating is increasingly used to plate automobile parts or household electric appliances. Among them, an ABS resin (acrylonitrile-butadiene-styrene copolymer) is formed into a molded product, and then a metallic film is formed on the surface of the molded product.

[Problems to be Solved by the Invention]

[0003] Electroless plating is completed by immersing the material into a plating solution after subjecting it to degreasing, etching and neutralizing processes. However, since chromic acid, sulfuric acid, and the like are used in

the etching process, the treatment of chromium oxide waste liquid is required in the neutralizing process as well as the etching process. In particular, since chromic acid can cause serious environmental pollution, first, the discharged chromium oxide waste liquid is acidified using sulfuric acid, the chromium oxide is reduced into hexavalent chromium and trivalent chromium in the waste liquid using a reductant, such as sodium hyposulfite, sodium sulfite, or the like, and then alkaline substances and a small amount of a coagulating agent are added to the waste liquid to separate a precipitate. For this reason, in the conventional electroless plating, complicated processes must be conducted as above.

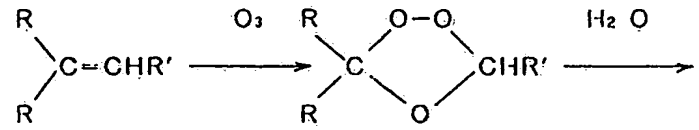
[0004] An object of the present invention is to provide a method of pretreating an electroless plating material without treating chromium waste liquid, which does not cause environmental pollution.

[Means for Solving the Problems]

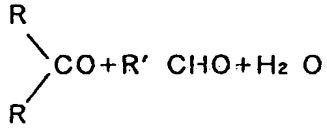
[0005] In order to accomplish the above object, the present invention provides a method of pretreating an electroless plating material in which an etching process in electroless plating is performed in combination with ozone treatment and sulfuric acid treatment without using acid. Among oxidants, ozone has the strongest oxidizability next

to fluorine, and is a gas at room temperature. Generally, silent discharge can be used in order to generate ozone. In the silent discharge, when high alternating voltage (for example, 10~15kV) is applied between metal electrode plates which are opposite each other through a dielectric material (for example, glass plate), silent discharge continuously occurs between the dielectric material and the metal electrode plates. At this time, when oxygen or dry air is applied into an electric field in which this silent discharge occurs, oxygen is converted into ozone. Generally, ozone is obtained in the form of a mixture of ozone and oxygen or a mixture of ozone and air.

[0006] When ozone is applied to a saturated organic compound, ozonide is produced. Therefore, when the ozonide is decomposed in the presence of water etc., the bond of the unsaturated portion of the ozonide is cleaved, and thus aldehydes, ketones, carboxylic acid, and the like are produced, as represented by the following Chemical Formula.



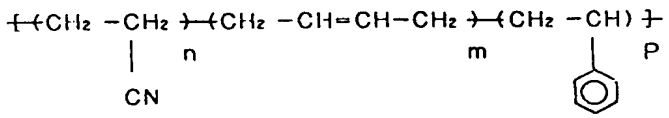
ozonide



[0007] This reaction progresses rapidly as the reaction temperature is increased. However, since ozone is an unstable material, and is characterized in that it returns to oxygen by autolysis, it is autolyzed at high temperature, and thus becomes inactive. Further, since the resin used for the electroless plating material has a specific softening temperature, it is deformed when the reaction temperature exceeds the specific softening temperature. Therefore, it is preferred that the electroless plating material be heated to a temperature of about 70~150℃. Further, when ultraviolet radiation, particularly, ultraviolet radiation having a wavelength of 253.7 nm, is absorbed in ozone, ozone is decomposed, but at the same time, activated oxygen O is generated. Since this activated oxygen has strong oxidizability, the chemical reaction of the ozone and resin rapidly proceeds. Accordingly, the ozone and resin more rapidly react with each other in the presence of ultraviolet irradiation, so that the surface of the resin loses smoothness, with the result that the surface of the resin is roughened.

[0008] Meanwhile, as described above, recently, synthetic resins have been chiefly used to manufacture automobiles or household goods, but an ABS resin is generally used as the electroless plating material. However, since this ABS resin has a monomer structure and an unsaturated bond as shown the

following Chemical Formula, it is converted into a low molecular resin by reacting it with ozone and then cleaving it.



For this reason, various molecules having different chemical compositions are mixed in the surface of the ABS resin, so that the surface of the ABS resin loses smoothness, with the result that the surface of the ABS resin is roughened. Therefore, when electroless plating is conducted on the roughened surface of the ABS resin, as described above, a metallic film deeply infiltrates into the roughened surface thereof, and is thus not easily peeled therefrom. Further, when the ABS resin is washed with sulfuric acid after the ozone treatment, the roughness of the surface of the ABS resin is increased to a greater extent due to variable sulfuric acid resistance, and thus a plated layer is not peeled from the surface of the ABS resin.

[Examples]

[0009] [Example 1]

Hereinafter, the present invention will be described in detail using ABS as a plating material.

First process: degreasing process

A plating material was electroless-plated, and the surface of the plating material was sufficiently cleaned. Grease was preliminarily removed from the surface of the plating material using a mixed solution of sodium sulfate, sodium phosphate and a surfactant, and then the plating material was washed with water.

Second process: etching process through ozone treatment

The plating material was put into a container at about 100℃ to make the temperature of the plating material uniform, and then ozone having a concentration of $100g/m^3$ was injected into the container. In a conventional etching process, for example, an ABS resin was immersed into a mixed solution of chromic acid and sulfuric acid, which was heated to a temperature of 65~75℃, and thus the surface of the ABS resin was chemically roughened. Although fine polybutadiene particles were dispersed near the surface of the ABS resin in a matrix phase at $10^3 \sim 10^4$Å intervals, they were dissolved in an etchant by performing the etching process, with the result that innumerable fine recesses are formed on the surface of the ABS resin. When a plated layer is formed on the surface of this ABS resin, the plated layer is mechanically bonded with the ABS resin by a so-called anchor effect, and thus it is difficult to peel the plated layer from the ABS resin. This effect is accomplished by ozone treatment, and thus a neutralizing process is not required.

Third process: plating process

In the case of nickel plating, as a plating solution into which a plating material is immersed, a pure solution, such as a nickel sulfate solution, a sodium hypophosphite solution, a citric acid solution or the like, is used. The formation rate of the plated layer is determined by the temperature of the plating solution and the immersion time of the plating material.

[0010] Ozone treatment and anchor effect

A resin test piece t, which was put into a container of about 100℃, having a size of 30×100×1mm, was etched by bringing a mixed gas of ozone and oxygen, having an ozone concentration of 100g/m^3, into contact with the resin test piece at a flow rate of 10 l/min, and then the etched resin test piece was nickel-plated.

[0011] [Example 2]

An ABS resin was used as a plating material as in Example 1.

First process: the first process of Example 2 is the same as that of Example 1.

Second process: A plating material t having a size of 30×100×1mm was etched by bringing a mixed gas of ozone and oxygen, having an ozone concentration of 100g/m^3, into contact with the plating material at a flow rate of 10 l/min in a container provided therein with a mercury lamp using

ozone and ultraviolet and then lighting the mercury lamp. Third process: the plating process of Example 2 is the same as that of Example 1.

[0012] [Example 3]

An ABS resin test piece was treated using the same method as in the first and second processes of Example 2, and was then treated with concentrated sulfuric acid before the third process was conducted, so as to increase the etching effect. Subsequently, the ABS resin test piece was nickel-plated using a general plating method in the third process.

[0013] The adhesive strengths of the plating materials of the above Examples due to the anchor effect were compared with those of the conventional plating materials etched using inorganic acid, and the results thereof are given below.

	adhesive strength (kg/cm)	conventional adhesive strength (kg/cm)
Example 1	1.0 - 2.0	1.0 - 3.0
Example 2	1.2 - 2.5	
Example 3	1.5 - 3.0	

[0014] [Advantages]

As described above, according to the present invention,

since harmful materials, such as chromium waste liquid and the like, are not used, electroless plating can be easily conducted without causing environmental pollution.